

# Binary metal oxides supported on $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for application in transesterification of low-grade cooking oil

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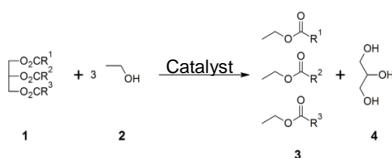
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## Graphical abstract



1. Triglycerides
2. Methanol
3. Fatty acid methyl ester (FAME)
4. Glycerol

## Abstract

Recently, the production of biodiesel has increased greatly due to the less harmful effects of this fuel towards the environment which is sourced from renewable materials compared to a conventional diesel. The aim of this study is to produce biodiesel using low-grade cooking oil by heterogeneous base catalyzed transesterification reaction. The series of solid base catalysts, binary metal oxide (Cu/Zn) were synthesized by the modified wet impregnation method supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The investigation of Cu/Zn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst on the calcination temperature, copper loading and number of alumina coatings had significantly affected the catalytic performance. The optimum conditions from experimental data were achieved with 10 wt% of Cu loading of Cu/Zn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 800°C with 3 times number of alumina coatings exhibited the highest fatty acid methyl ester (FAME) yields, 87.07% at mild reaction conditions (65°C, atmospheric pressure, 1:20 methanol-to-oil molar ratio, 10 wt% of catalyst loading and 2 hours of reaction time). The physicochemical properties studied by BET surface area of Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 800°C which gave high surface area, 149.32 m<sup>2</sup>/g. FESEM-EDX analysis of Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst indicated the amorphous in structure with undefined shapes and mixture of larger and smaller particles sizes. The production of biodiesel and the percentage conversion of FAME was analyzed by using GC-FID in the presence of methyl palmitate, cis-9-oleic acid methyl ester and methyl linoleate.

**Keywords:** Binary metal oxides, biodiesel, transesterification, catalytic performance

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## INTRODUCTION

Recently, the depleting of the earth's finite resource such as fossil fuel and the emissions of greenhouses gases in the environment is unsustainable that lead to the much interest in converting biomass resources into biodiesel as an alternative substituted energy (Hameed *et al.*, 2009; Atadashi *et al.*, 2011; Nakatani *et al.*, 2009). As the world is experiencing rapid social, economic and environmental transformation, many researchers are study on topic of biodiesel production and development.

Biodiesel which recognised as a fatty acid methyl ester (FAME) is known as a clean-burning fuel, since it is biodegradable, nontoxic, sulfur and aromatic-free that produce less air pollutants in comparison with petroleum-based fuels (Nas and Berkday, 2007). This new source of energy can be derived from renewable resources such as vegetable oils including palm, sunflower, rapeseed, canola and soybean oil (Granados *et al.*, 2007; MacLeod *et al.*, 2008).

Several modification techniques have been developed to biodiesel production and application such as direct use of vegetable oil, microemulsions, pyrolysis and transesterification (Farobie and Matsumura, 2015; Shuit *et al.*, 2012; Avhad *et al.*, 2015). Recently efforts have been focused on the use of heterogeneous catalysts due the simplifying of biodiesel production and purification steps resulted in declining amount of waste water (Gao *et al.*, 2009). The heterogeneous catalysts that most commonly used in transesterification of biodiesel are single metal oxides such as calcium oxide, zinc oxide, magnesium oxide and inorganic compound due to its cheap price, relatively high basic strength and less environmental impacts.

Much interest has been taken in the application of structure promoters or catalyst supports which can provide more specific surface area and pores for active species (Zabeti *et al.*, 2009). Furthermore, to increase the basic strength of a single metal oxide, mixed metal oxides are synthesized. Therefore, in this study, the modification with more active substance in order to prepare a base heterogeneous catalyst was introduced in biodiesel production due to the environmental constraints and simplifications in the existing process. This modified base heterogeneous catalyst, Cu/Zn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> which are non-leaching and recyclability for the transesterification of biodiesel has not been revealed.

## EXPERIMENTAL

### Materials

Zinc nitrate hexahydrate, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, copper(II) nitrate trihydrate, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, gamma-alumina oxide (beads),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, methanol, CH<sub>3</sub>OH and *n*-hexane, C<sub>6</sub>H<sub>14</sub> were purchased from Merck. All chemicals and solvents were used without further purification. The low-grade cooking oil was obtained from local market.

### Catalyst preparation

The bimetallic oxides catalysts were prepared by using wet impregnation method supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (specific area 253 m<sup>2</sup>/g and 3-5 mm diameter). Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O as a dopant was dissolved into 5 mL of distilled water according to the dopant ratio to based. About 5.0 g of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O as a based metal oxides were dissolved into 5 mL of distilled water. Both based and dopant solutions were mixed and

dissolved together. Then, 5.0 g of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> that is most widely used as support material was dipped into precursor solution within 1 hour varied with 1 to 5 times of coating respectively. After coating,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> beads were aging at ambient room temperature and followed by at temperature of 80 to 90°C in the oven for 24 hours to remove water and to allow good coating of the metal on the surface of the supported catalysts. Then, the samples were calcined at temperature of 700, 800 and 900°C for 5 hours using a ramp rate of 5°C/min to eliminate all the metal precursor impurities.

### Catalyst characterization

The prepared catalysts were characterized using Brunauer Emmett Teller (BET), Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray (EDX). The nitrogen adsorption analysis of the catalyst was studied using Micromeritics ASAP 2010. Prior to analysis, the 0.2-0.3 g of powder sample was degassed at 120°C to remove the previously adsorbed gasses and evacuating the dead space by vacuum pump to cool at room temperature. The specific surface area was calculated from the adsorption curve according to the Brunauer–Emmett–Teller (BET) method.

FESEM-EDX analysis was accomplished by using Philips XL 40 microscope with energy of 15.9 kV coupled with EDX analyser and bombarded using electron gun with tungsten filament under 25 kV resolutions to get the required magnification image. EDX was used in this study to determine the elemental composition on the submicron scale. The supported catalyst sample was attached by carbon tape on special platform called stub, coated with platinum using a platinum sputter at 10<sup>-1</sup> Mbar using a Bio Rad Polaron Division SEM coating system machine. The sample was bombarded using an electron gun with a tungsten filament under 25 kV resolutions in order to get the required magnification image.

### Catalytic reaction and product analysis

About 1.2 g of the prepared catalyst, 18.5 g of methanol and 20.0 g of low-grade cooking oil were added into a two-necked round bottom flask and refluxed at 65 ± 5°C for 3 hours to complete the transesterification reaction. The mixture was centrifuged at 3000 rpm for 10 min to separate the solid catalyst from the solution. Three layers were obtained after the centrifugation. An excess of methanol at the top layer, a biodiesel at middle layer and the bottom layer was catalyst samples and glycerol. The biodiesel was collected for further characterization. The experiment was repeated by using different percentages catalyst loading (2 to 13 wt%), reaction time (1 to 5 hours) and oil to methanol ratio (1:12 to 1:24) to obtain optimum reaction conditions for biodiesel production.

The product obtained was analyzed using GC-FID, equipped with a SP-2560 capillary column (100 m x 0.25 mm x 0.20 µm) and helium as a carrier gas. The column temperature program was as follows: the initial temperatures was 140°C for 5 min and the first rate was 4°C/min up to 240°C for 15 min. The injector and detector temperatures was set up at 260°C.

## RESULTS AND DISCUSSION

### Catalytic activity tests

The synthesized binary metal oxides catalysts, Cu/Zn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were tested in the transesterification reaction of low-grade cooking oil at identified reaction conditions which were reaction temperature of 65°C, oil to methanol ratio of 1:24, reaction time of 3 hours and catalyst loading of 6 wt%. The series of Cu/Zn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were varied with the different calcination temperatures (700 to 900°C), percentage of Cu loading (5 to 30 wt%) and number of alumina coatings (1 to 5 dip). The optimum conditions from experimental data were achieved with 10 wt% of Cu loading of Cu/Zn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 800°C with 3 times number of alumina coatings exhibited the highest fatty acid methyl ester (FAME) yields, 87.07% due to the most optimum active sites strength for biodiesel reaction. Based upon the experimental results, Cu/Zn (10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 800°C was selected for further studies to optimize the biodiesel production from low-grade cooking oil.

### Catalyst characterization

#### Brunauer Emmett Teller (BET)

Table 1 shows the specific BET surface area,  $S_{BET}$  of Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts at different calcination temperatures. It was found that increasing the calcination temperature could increase the surface area. The Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 800°C gave the highest BET surface area of 149.32 m<sup>2</sup>/g as compared to the catalysts calcined at 700°C which gave of 146.77 m<sup>2</sup>/g.

This observation was expected due to the catalytic testing which the Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 800°C was more active during the reaction as it was able to convert a maximum 87.07% of biodiesel. The BET surface area decreased drastically to 53.09 m<sup>2</sup>/g when the catalyst was calcined at 900°C due to the partially collapsed of the pore structure after its contact with the catalyst at the higher calcination temperature. It will lead to the increasing of particle size of the catalyst and thus, surface area will be reduced (Rao *et al.*, 2011)

Therefore, Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> calcined at 800°C was the potential catalyst due to its high surface area that will lead to a rise in the number of active sites. Based on the catalytic activity, the Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was more active during the reaction at temperature of 800°C as it was able to convert a maximum of 87.07% fatty acid methyl esters yield.

**Table 1** The specific BET surface area,  $S_{BET}$  or Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst calcined at different temperatures for 700, 800 and 900°C for 5 hours.

Catalyst	Calcination Temperature (°C)	BET Surface Area (m <sup>2</sup> /g)
Cu/Zn(10:90)/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	700	146.77
	800	149.32
	900	53.09

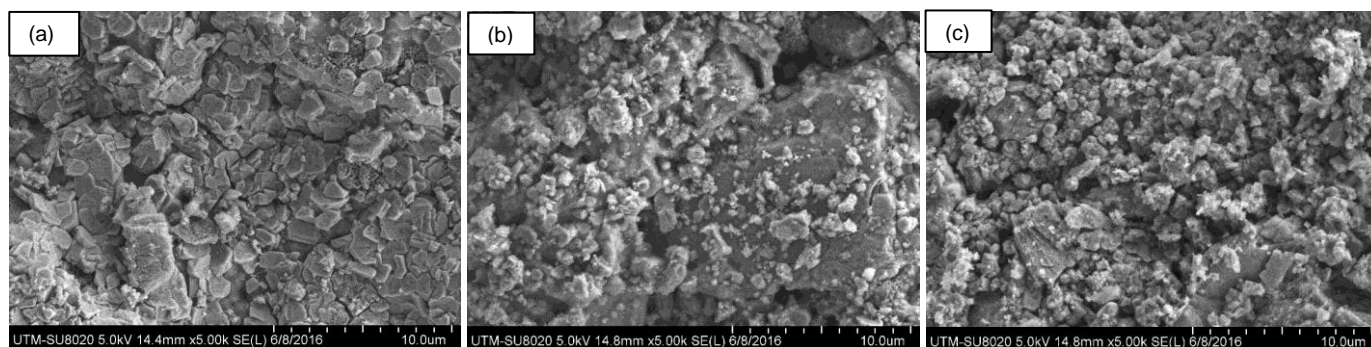
#### Field Emission Scanning Electron Microscopy (FESEM)

Figure 1 shows that an increase in calcination temperature from 700 to 800°C leads to the formation of aggregates with undefined shapes and mixture of larger and smaller particles size. Such morphology of Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 800°C should provide the space for the access of active metal components to attract hydrogen molecules on the catalyst surface.

However, when the calcination temperature reached at 900°C, it showed more agglomeration and their catalyst surfaces were densely packed. It is due to the sintering effect that occurred during the calcination process hence form larger particle size. It was expected that the dense packed surface of catalyst leads to the reduction of surface area as well as the catalytic activity performance. Oh *et al.* (2007) and Rosid *et al.* (2014) proposed that the well-defined morphology of the catalyst surface was highly correlated with the calcination temperatures of catalysts.

#### Energy Dispersive X-ray (EDX)

Table 2 shows the chemical compositions expressed as weight percentage over Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst obtained from EDX analysis. The composition of the Al was determined to be around 46.00 – 49.00 wt% over all the catalysts prepared. Meanwhile, the composition of Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst calcined at various calcination temperatures showed slight differences with its original composition. The detected Cu content decreased from 3.90 wt% at temperature of 700°C to 2.00 wt% at temperature of 800°C and increased to 3.60 wt% at calcination temperature of 900°C. This was probably due to the increase of particles size and the agglomeration of Cu particles that occurred on the surface of the catalyst after being calcined at higher temperature (Abdullah *et al.*, 2014). As can be seen, Cu and Zn elements in Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> calcined at 800°C was lower due to the well-distributed on the surface of the catalyst representing that the catalyst has a higher dispersion. Therefore, the calculated area was mainly packed with the Al and O component respectively.



**Fig. 1** FESEM micrographs of Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst calcined at temperatures of (a) 700°C, (b) 800°C and (c) 900°C for 5 hours with magnification 5000 and scale bar 10  $\mu$ m.

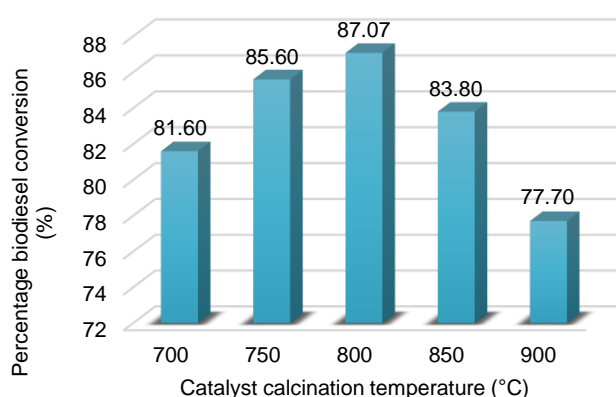
**Table 2** Elemental composition by EDX analysis of Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst calcined at different temperatures for 700, 800 and 900°C for 5 hours.

Catalyst	Calcination Temperature (°C)	Loading (wt%)			
		Al	O	Cu	Zn
Cu/Zn(10:90)/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	700	46.00	39.70	3.90	10.20
	800	48.90	43.40	2.00	5.70
	900	48.00	39.70	3.60	8.70

### Catalytic reaction and product analysis

#### Effect of calcination temperature on Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

Figure 2 shows the effect of calcination temperatures of Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 700 to 900°C respectively. From the catalytic activity, it revealed that Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 800°C was the optimum calcination temperature with 87.07% conversion of biodiesel. The catalytic activity increase up to 800°C and slightly decreased at calcination temperature of 900°C. Based on Figure 2, the catalytic activity of Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 800°C was the best catalyst for transesterification reaction of low-grade cooking oil to biodiesel compared to the others. According to Wachs (1996), the high calcination temperature assures that the surface metal oxides are fully oxidized and dispersed that leads to the formation of solid solution was avoided.



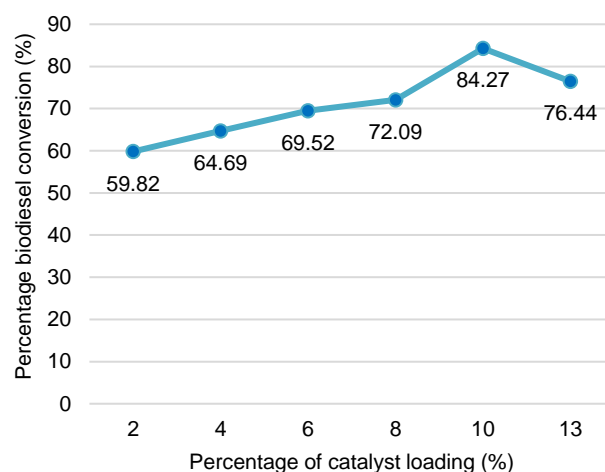
**Fig. 2** The effect of calcination temperatures of Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 700, 800 and 900°C for 5 hours respectively.

#### Effect of percentage of catalyst loading

Figure 3 illustrates the effect of catalyst loading towards percentage conversion of biodiesel using Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as catalyst. Catalyst amount is one of the most important factors that affect the biodiesel production in the transesterification reaction. From previous study, it showed that different amounts of catalyst loading affect the percentage conversion of biodiesel (Wang and Yang, 2007). Based on

Liu *et al.*, (2008), a catalyst possessing a strong basic site and a large surface area should give higher activity. The effect of the catalyst amount with biodiesel production was studied by varying wt. % loading of Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst which were 2 to 13 wt% respectively with 3 hours reaction time.

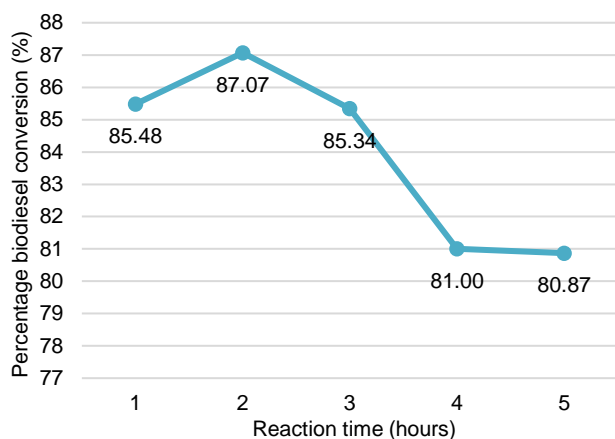
Based on these result, it showed that 10 wt% catalyst loading performed the optimum percentage conversion of biodiesel, 84.27%. The percentage yield was increased with the increasing of catalyst loading because the catalyst provides more active sites for reaction. This suggested that at 10 wt% catalyst loading contact between the reactants and solid catalyst was maximum which directly influenced the forward transesterification reaction speed, thus provided maximum biodiesel yield. For the 2 wt% catalyst loading, the percentage conversion of biodiesel was low with only 59.82% due to the less active surface area of catalyst present. It gave lower defect sites that could decrease the conversion of biodiesel. When 13 wt% catalyst loading was applied in the reaction, the percentage conversion of biodiesel was decreased at similar reaction conditions. This was due to the mixing problems of the reaction mixture involving reactants, products and solid catalyst.



**Fig. 3** Percentage biodiesel conversion with different loading of Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 800°C for 5 hours respectively.

#### Effect of reaction times

Figure 4 shows the effect of reaction time towards the percentage conversion of biodiesel with 10% of catalyst loading. It showed that the percentage conversion was increased with increasing the reaction time from 1 to 2 hour. The rate of transesterification reaction is strongly influenced by the reaction time. The conversion increased progressively with increasing reaction time and then reached optimum value representative of a nearly equilibrium conversion. Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst gave a maximum conversion at 2 hour reaction time was 87.07%. After 2 hour reaction time, the biodiesel yield was decreased due to reverse reaction which was the formation of triglycerides.

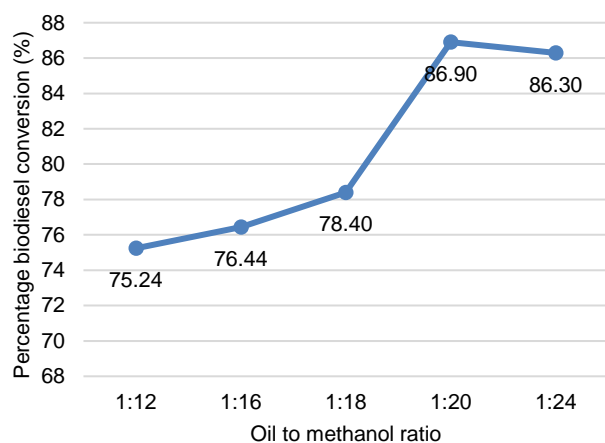


**Fig. 4** Percentage biodiesel conversion with different reaction time using Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 800°C for 5 hours respectively.

### Effect of oil to methanol ratio

The transesterification process consists of a sequence of three consecutive reversible reactions where the triglyceride is successively transformed into diglyceride, monoglyceride, and finally into glycerin and the fatty acid methyl esters. The molar ratio of oil to methanol is one of the important factors that affect the conversion to methyl esters. Stoichiometrically, three moles of methanol are required for each mole of triglyceride, but in practice a higher molar ratio is employed in order to drive the reaction towards completion and produce more methyl esters as products.

Figure 5 illustrates the effect of oil to methanol ratio towards conversion of biodiesel. As shown in this figure, with an increase in the methanol-loading amount, the conversion was increased considerably. The maximum conversion was obtained when the molar ratio was 1:20. However, the excessively added methanol had no significant effect on the conversion. Therefore, the optimum molar ratio of oil to methanol to produce methyl esters was 1:20 with 86.90%.



**Fig. 5** Percentage biodiesel conversion with different oil to methanol ratio of Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 800°C for 5 hours respectively.

### CONCLUSION

As a conclusion, the optimum conditions for transesterification reaction was achieved 10 wt% catalyst loading at 2 hours reaction times with 1:20 wt% methanol to oil ratio which gave the highest percentage yield of biodiesel, 87.07% using Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as catalyst. The best conditions for catalyst obtained with 3 times number of alumina

coatings, 10:90 dopant ratio to based and calcined at temperature of 800°C. The physicochemical properties studied by BET surface area supported the results of Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 800°C which gave high surface area, 149.32 m<sup>2</sup>/g, that influenced the catalytic activity of transesterification process. FESEM-EDX analysis of Cu/Zn(10:90)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst indicated the amorphous in structure with undefined shapes and mixture of larger and smaller particles sizes.

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### REFERENCES

- Abdullah, W. N. W., Bakar, W. A. W. A. and Ali, R. 2015. Catalytic oxidative desulfurization of diesel fuel utilizing a polymolybdate alumina supported catalyst: Characterization, catalytic activity and mechanistic study. *React. Kinet. Mech. Catal.* 114. 547-560.
- Atadashi, I., Aroua, M., Aziz, A. and Sulaiman, N. 2011. Membrane biodiesel production and refining technology: A critical review. *Renew. Sustain. Energy Rev.* 15. 5051-5062.
- Avhad, M.R. and Marchetti, J. M. 2015. A review on recent advancement in catalytic materials for biodiesel production. *Renew. Sustain. Energy Rev.* 50. 696-718.
- Farobie, O. and Matsumura, Y. 2015. A comparative study of biodiesel production using methanol, ethanol, and tert-butyl methyl ether (MTBE) under supercritical conditions. *Bioresour. Technol.* 191. 306-311.
- Gao, Y., Chen, W., Lei, H., Liu, Y., Lin, X. and Ruan, R. 2009. Optimization of transesterification conditions for the production of fatty acid methyl ester (FAME) from Chinese tallow kernel oil with surfactant-coated lipase. *Biomass Bioenergy.* 33. 277-282.
- Granados, M., Poves, M., Alonso, D. M., Mariscal, R., Galisteo, F. and Moreno-Tost, R. 2007. Biodiesel from sunflower oil by using activated calcium oxide. *Appl. Catal. B Environ.* 73. 317-326.
- Hameed, B.H., Goh, C.S. and Chin, L.H. 2009. Process optimization for methyl ester production from waste cooking oil using activated carbon supported potassium fluoride. *Fuel Process Technol.* 90. 1532-1537.
- Liu, X., He, H., Wang, Y., Zhu S. and Piao, X. 2008. Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. *Fuel.* 87. 216-221.
- MacLeod, C., Harvey, A. P., Lee, A. F. and Wilson, K. 2008. Evaluation of the activity and stability of alkali-doped metal oxide catalysts for application to an intensified method of biodiesel production. *Chem. Eng. J.* 135. 63-70.
- Nakatani, N., Takamori, H., Takeda, K. and Sakugawa, H. 2009. No transesterification of soybean oil using combusted oyster shell waste as a catalyst. *Bioresour. Technol.* 100. 1510-1513.
- Nas, B. and Berktaay, A. 2007. Energy potential of biodiesel generated from waste cooking oil: an environmental approach. *Energy Sources B Econ. Plan. Policy.* 2. 63-71.
- Oh, S. W., Bang, H., Bae, Y. C. and Sun, Y. K. 2007. Effect of calcinations temperature on morphology, crystallinity and electrochemical properties of nanocrystalline metal oxides (Co<sub>3</sub>O<sub>4</sub>, CuO and NiO) prepared via ultrasonic spray pyrolysis. *J. Power Source.* 17. 502-509.
- Rao, K. N., Venkataswamy, P. and Reddy, B. M. 2011. Structural characterization and catalytic evaluation of supported copper-ceria catalysts for soot oxidation. *Ind. Eng. Chem. Res.* 50. 11960-11969.
- Rosid, M. S. J., Bakar, W. A. W. A. and Ali, R. 2014. Physicochemical study of supported cobalt-lanthanum oxide-based catalysts for CO<sub>2</sub>/H<sub>2</sub> Methanation Reaction. *Clean Technol. Envir.* 17. 627-636.
- Shuit, S., Ong, Y., Lee, K., Subhash, B. and Tan, S. 2012. Membrane technology as a promising alternative in biodiesel production: a review. *Biotechnol. Adv.* 30. 1364-1380.
- Wachs, I. E. 1996. Raman and IR Studies of Surface Metal Oxide Species on Oxide Supports: Supported Metal Oxide Catalysts. *Catal. Today.* 27. 437-455.
- Wang, L. and Yang, J. 2007. Transesterification of soybean oil with nano-MgO or not in supercritical and subcritical methanol. *Fuel.* 86. 328 - 333.
- Zabeti, M., Daud, W. M. A. W. and Aroua, M. K. 2009. Optimization of the activity of CaO/Al<sub>2</sub>O<sub>3</sub> catalyst for biodiesel production using response surface methodology. *Appl. Catal. A Gen.* 366. 154-159.